IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

Ex Parte KEVIN CINK, JEFFREY C. SMITH, JAMES NANGERONI AND JED RICHARD RANDALL

Application 10/593,111

Art Unit: 1796

BRIEF ON APPEAL

This brief on appeal is being filed pursuant to 37 CFR §41.37. The fee set forth in 37 CFR §41.20(b)(2) accompanies this paper.

Real Party at Interest

The real party at interest in this case is NatureWorks LLC, assignee of record.

Related Appeals and Interferences

There are no related appeals, interferences or other judicial proceedings known to appellant, the undersigned legal representative of appellant or the assignee which may be related to or have a bearing on the Board's decision on the pending appeal.

Status of Claims

The status of the claims of this application is as follows:

Rejected claims that are subject of this appeal: 24, 27-32.

Canceled claims: 1-23.

Claims withdrawn from consideration: 25, 26.

Status of Amendments

There were no amendments after the final rejection.

Summary of Claimed Subject Matter

The application contains a single independent claim, claim 27.

As defined in claim 27, the invention is a process that comprises forming a pressurized, molten mixture of a melt-processable polylactide resin (specification page 2 lines 11-13) containing about 5 to about 15% by weight, based on the weight of the polylactide resin, of carbon dioxide (specification page 2 lines 13-14 and page 5 lines 30-32). The molten mixture is extruded at an extrusion temperature through a die to a region of reduced pressure such that the carbon dioxide expands and the polylactide resin simultaneously cools to form a stable foam (specification page 2 lines 14-16, page 6, lines 21-24, page 7 lines 9-11). The extruded foam has at least 70% closed cells (specification page 9 lines 25-28). The polylactide resin contains at least 80% by weight polymerized lactic acid units (specification page 3 lines 2-3).

Grounds of Rejection to be Reviewed on Appeal

The grounds of rejection to be reviewed are:

1. The rejection of claims 24, 27-30 and 32 under 35 USC §103(a) as obvious over US 5,134,171 (Hammel) in view of JP 2003-073495 (Shinohara).

2. The rejection of claim 31 under 35 USC §103(a) as obvious over US 5,134,171 (Hammel) in view of JP 2003-073495 (Shinohara) and further in view of US 5,238,968 (Morita).

Argument

1. The technological background of this invention.

This invention relates to a method of extruding polylactide resins to make closed-cell foams.

Two important manufacturing methods for making polymer foams are the extrusion method and the bead foam method. In the former method, a polymer is melted and combined with a blowing agent in an extruder. The extruder is pressurized to prevent the blowing agent from escaping. The pressurized blowing agent mixture is then expelled

through a die to a region of reduced (usually atmospheric) pressure. The polymer expands and simultaneously cools to form a stable foam.

The product of an extrusion process is in most cases a single mass of cellular polymer. It has a uniform cross-section, due to the expansion process, and may be shaped into specialized parts using various fabrication methods. The process is well-adapted for making large parts or high volume parts.

The bead foam process is dramatically different. In the bead foam process, the polymer is formed into small beads. The beads are impregnated with a blowing agent, taking care not to melt or soften them (lest they lose their particulate form). Moldings are made from these beads by pouring them into a mold and then heating them, without applied pressure, enough to expand the blowing agent. The beads are softened enough that they can be expanded with the blowing agent, and so they stick together. The products from the bead-foam processes are easily recognized, because the bead structure is usually still visible in the molded product. The bead foam process is often used to make small molded articles or articles with complex shapes that cannot be made easily by extrusion or by fabricating an extruded foam.

Many types of common thermoplastics cannot be processed easily in an extrusion foaming process. To be operated successfully, an extrusion foaming process requires that the polymeric material have certain rheological properties, which are often referred to as melt strength. Resins like polylactides have low melt strength, and are difficult to manage in an extrusion foaming process. Operating windows are so small that it becomes impossible as a practical matter to operate a commercial scale production line, because process conditions are difficult to maintain within those small windows.

The usual approach to resolving the problem of low melt strength is to introduce long-chain branching into the resin or to increase molecular weight. In the case of polylactides, however, this has not been entirely suitable, and in addition requires one to develop specialty resin grades for extrusion foaming application.

A number of blowing agents have been tried in polylactide foam extrusion processes. These include carbon dioxide, nitrogen and various hydrofluorocarbons, as shown in the Hammel reference relied upon by the examiner. Because carbon dioxide has a lower molecular weight than most other blowing agent candidates, only small amounts of it have been needed to expand the foam. In the Hammel reference, carbon dioxide is described as being used at the 0.44% by weight level (based on resin). Another reference, JP 2002-

322,309A, describes an attempt to use carbon dioxide at the 4.5% by weight level, but the foam collapsed.

2. The present invention.

This invention is a process for extrusion foaming a polylactide that contains at least 80% by weight polymerized lactic acid units. A mixture of the polylactide and carbon dioxide are formed into a pressurized molten mixture. This mixture is then extruded through a die into a region of reduced pressure, at which point the carbon dioxide expands and the polylactide simultaneously cools. This produces a stable foam that has at least 70% closed cells.

An important feature of this invention is the amount of carbon dioxide, which is extremely high, much greater than what is needed simply to expand the polymer to the desired density. In this process, from 5 to 15% of carbon dioxide is present in the molten mixture.

Several advantages accrue with the use of the high carbon dioxide levels. Very low density foams can be produced, and those foams have good cell structure, good appearance and, very importantly, consistent quality. The process operates well even with polylactide resins that are low in melt strength, and so the process has the benefit of working well using even general-purpose grades of polylactide. In addition, the presence of high levels of carbon dioxide appears to plasticize the molten resin, affecting its melt rheology and allowing lower extrusion temperatures to be used. Lower extrusion temperatures are desirable because (1) melt viscosities are lower at those temperatures, which favors a stable foaming process and (2) the resin exiting the die is closer to its glass transition temperature, and so can solidify rapidly upon expansion, before the blowing gases can escape.

3. The cited prior art

The primary reference in these rejections on appeal is USP 5,134,171 to Hammel.

Hammel describes a process whereby a polyhydroxy acid polymer is foamed using environmentally benign blowing agents (abstract). Polylactic acid is a preferred polyhydroxy acid polymer (column 3 line 11). (Note: for purposes of this discussion, "poly(lactic acid)" and "polylactide" can be and are used interchangeably.) The blowing agents include nitrogen, carbon dioxide and certain hydrofluorocarbons (column 3 lines 26-

35). An extrusion foaming process is described (column 6 lines 14-20, Examples 1-8). The resulting extruded foam can have 90% or more closed cells (column 3 lines 43-45). The extruded foam can be hot formed into desired shapes, such as plates (column 6 lines 56-57 and example 1).

Example 8 of Hammel describes an extrusion foaming process, using poly(lactic acid) as the resin and carbon dioxide as the blowing agent. The weight ratio of carbon dioxide to poly(lactic acid) resin in this example is 2.16 pounds of carbon dioxide per 495.34 pounds of resin. This comes to 0.44% by weight of carbon dioxide based on the weight of the resin.

Hammel's Example 8 is the only teaching in the reference that relates to the quantity of carbon dioxide to be used in an extrusion foaming process.

JP 2003-073495 (Shinohara) is cited as a secondary reference. Unlike Hammel, and contrary to the examiner's characterization, Shinohara relates to a bead foaming process, not any type of extrusion process, as will now be explained.

In Shinohara's process, a polylactic acid is formed into small particles. This can be done be extruding the resin into a strand, and then fracturing the strand into small pieces (paragraph [0011]). The examiner cites paragraph [0011] in support of her position that Shinohara describes extrusion foaming. However, the extrusion step described in paragraph [0011] is *not* conducted in the presence of any blowing agent, as is required by applicants' claims and as is characteristic of an extrusion foaming process. Instead, Shinohara's extrusion step is used solely to produce polymer particles which are impregnated with blowing agent in a subsequent step (paragraph [0016]).

Shinohara impregnates the particles with carbon dioxide (paragraph [0017]). Up to 20% of carbon dioxide can be used in the impregnation step (paragraph [0017]). The impregnation step is performed at a controlled temperature, which depends on the amount of carbon dioxide to be impregnated. The temperature range for the impregnation step is given by the expression

$$3 < \text{ambient temperature} < -2.5X + 55$$

where X is the carbon dioxide concentration and "ambient temperature" is the temperature in °C at which Shinohara's beads are impregnated. Note that the ambient temperature can never be above 55°C, according to Shinohara. At a carbon dioxide concentration of 5% (the lowest permitted by applicant's claims), the ambient temperature according to Shinohara cannot exceed 42.5°C. Both 55°C and 42.5°C are well below the softening and melting

temperatures of PLA resins. PLA cannot be extruded at such low temperatures. Therefore, Shinohara's impregnation step is different from applicants' melt extrusion process.

Finally, Shinohara expands the impregnated particles to produce molded foam articles. This is done by placing the particles into a mold and applying heat (paragraph [0019]). Shinohara is careful to say that the particles are "softened" in this step, rather than "melted" (paragraph [0019], line 5). The temperature during this step is no greater than 60°C above the resin T_g (paragraph [0019], line 14-18), which means that the temperature during the molding step will be less than the crystalline melting temperature of the resin, which is at least 130°C, as reported at paragraph [0007]. (The T_g of polylactide resins is approximately 55-65°C, as reported in JP 2002-322,309A, paragraph [0010].) Shinohara explicitly reports that problems arise when using higher temperatures (paragraph [0019], final four lines). In addition, the mold is not pressurized; Shinohara describes venting the mold, so air can escape from the mold as the particles expand (paragraph [0019] lines 12-14). Therefore, Shinohara's molding step does not correspond to any extrusion foaming step such as is described in applicants' claim 27.

Shinohara mentions phenomena such as "weld nature" and "die shape reproducibility" (e.g., paragraph [0003]), and the examiner has seized upon those terms to conclude that Shinohara must be describing an extrusion foaming process. However, Shinohara unambiguously uses these terms to describe the results of a bead foaming process, not an extrusion foaming process. This is clearly shown by examining paragraphs [0032] and [0035]. Paragraph [0032] describes the normal process of making polymer beads, impregnating them with blowing agent and then molding and expanding the beads. This process is unambiguously a bead foaming process, not an extrusion foaming process. Paragraph [0035] discusses the results of the bead foaming process described in paragraph [0032]. There, "weld nature" is plainly mentioned as an attribute of the paragraph [0032] bead-foamed product, as is "die shape appearance".

USP 6,395,791 (Chaudary) is erroneously relied on by the examiner to establish a point of fact, *i.e.*, that foamable beads may be extrusion foamed to form various articles. The examiner cites to column 24 lines 38-48, column 25 lines 37-45 and column 28 lines 16-40, as allegedly showing that foamable beads are extruded. Column 24 lines 38-48 only describes molding the beads, not extrusion foaming them, and is entirely consistent with the Shinohara reference. Column 25 lines 37-45 describes an extrusion process for *making*

the foamable beads, not *expanding* them. Note in this respect that the resin in Chaudary is not a polylactide, as in Shinohara and as in the present invention. Furthermore, Chaudary's extrusion process for making the foamable beads is exactly contrary to the teachings of Shinohara. The extrusion process of Chaudary's column 25 lines 37-45 is a melt process, whereas Shinohara explicitly requires a maximum temperature during the impregnation step of 55°C, at which temperature the poly(lactide) will be in the form of solid particles.

Column 28 lines 16-40 of Chaudary only describes various types of products that can be made using Chaudary's foams; it does not describe any process in which foamable beads are extrusion foamed.

Morita (USP 5,238,968) describes an extrusion foaming process for making open-celled polylactide foam. A number of blowing agents are described, including reactive types, which are solids at room temperature (column 6 lines 13-20), volatile solvents (column 6 lines 23-28) and gases (column 6 lines 28-30). Among the possible gases is carbon dioxide. Blowing agents are described generally as being useful in ranges from 0.2 to 10% by weight (column 6 lines 31-35), but in citing this quantity, Morita does not attempt to make any specific teachings about how much of any specific type of blowing agents should be used. The only such specific teachings are in Morita's table 3, where azodicarboxylic acid amine, a solid reactive type of blowing agent, is used in amounts ranging from 0.1 to 15%. The examiner relies on Morita for its teachings regarding extrusion temperature, which are broadly described at column 6 lines 53-55 at being from 100 to 270°C.

JP 2003-073495 has been cited by the applicants as showing the state of the art. Comparative example 2 (paragraph [0041]) of this document describes an attempt to extrude poly(lactic acid) foam using 4.5% carbon dioxide as the blowing agent. In paragraph [0042], it is reported that the foam has an internal cavity and "the obtained foam did not turn into good foam".

<u>4. The invention of claims 27 and 32 is not obvious over the combination of Hammel and Shinohara</u>

As discussed above, Hammel fails to describe a polylactide extrusion foaming process, in which from 5 to 15% of carbon dioxide, based on the weight of resin, is used as

the blowing agent.

The only teaching that Hammel contains regarding carbon dioxide levels is in Example 8, in which the carbon dioxide concentration is only 0.44% by weight. This is only about 8% of applicants' minimum level. There is no suggestion to use any greater amount of carbon dioxide.

The examiner points to Hammel Example 1, in which a *different* blowing agent (HFC 134a) is used at the 5% level. From this example, the examiner alleges, with no basis at all, that it would have been obvious to use *any* blowing agent, including carbon dioxide, at the 5% level. However, Example 1 says nothing whatsoever about suitable amounts of carbon dioxide. Its teachings are pertinent solely to HFC-134a.

HFC-134a is a much heavier molecule than carbon dioxide; Hammel reports its molecular weight to be 102, vs. only 44 for carbon dioxide. It stands to reason that higher weight of HFC-134a would be needed to expand a foam, compared to carbon dioxide, because more weight is needed to provide an equivalent number of moles of expanding gas. And, in fact, the table at the top of Hammel column 7 bears this out. In that table, seven different blowing agents are described, which range in molecular weight from 28 (nitrogen) to 170 (HFC-227ea). The amounts of blowing agent that are used precisely track their respective molecular weights; the lightest blowing agent (nitrogen) is used in the smallest amount, and as molecular weights increase, blowing agent loadings increase correspondingly. The particular loadings in each case are approximately proportional to the molecular weight of the blowing agent.

Turning back to Example 1, a molar quantity of carbon dioxide equal to the molar quantity of HFC-134a would lead to a carbon dioxide concentration of only 2.16% (5% X 44/102 = 2.16%). Even if one were to make this sort of extrapolation from the reference, 2.16% is still only about 43% of applicant's minimum level. Of course, the reference says nothing about how, or whether, 2.16% carbon dioxide could be used to make good foam. All it says is that an equivalent molar amount of a different blowing agent can be used.

Therefore, when read as a whole, Hammel does not teach or suggest using at least 5% of carbon dioxide, but instead describes much lower quantities.

As already discussed, Shinohara does not describe any extrusion foaming process at all, and therefore provides no reason whatsoever to modify the teachings of the Hammel reference.

The conditions under which Shinohara's bead foaming process operates are so

different from those of an extrusion foaming process that the respective operations are simply not comparable. In the extrusion process, the resin and the blowing agent are formed into a molten mass within a pressurized extruder.

No such molten mass is ever formed in Shinohara's bead foaming process. Shinohara's temperature restrictions, in fact, explicitly prohibit the formation of any such molten mass. The maximum temperature in Shinohara's impregnation step is only 55°C, and the maximum temperature in Shinohara's molding step is below the crystalline melting temperature of the poly(lactic acid) resin. Each of these conditions precludes the formation of a molten mass of poly(lactic acid) resin and blowing agent.

No pressurized molten mass is ever formed in Shinohara's bead process, either. Shinohara's impregnation step is performed on polylactide *particles*, not in a melt. Shinohara's molding step is not performed under pressure; the mold is vented to allow gas to escape so the material can expand.

In the extrusion foaming process, the pressurized molten mass is passed through a die to a lower pressure region where the blowing agent expands and the polymer cools to form a stable foam. This does not occur in Shinohara's process, either. Shinohara's impregnated beads are never melted, never pass through a die, and are never brought from a pressurized condition to a region of lower pressure.

In the extrusion foaming process, the blowing agent expands as the polymer cools. This feature, too, is absent from Shinohara's bead foam process, as the expansion occurs during heating in a mold.

When the differences between the extrusion foaming and bead foaming processes are understood, it is easily seen that materials and conditions useful in a bead foam process have little relevance to an extrusion foaming process. In particular, the simultaneous expansion and cooling that occurs in the extrusion foaming process requires a delicate balance between blowing agent expansion and polymer cooling, so that the blowing agent does not simply escape, allowing the foam to collapse, or that the polymer does not harden so rapidly that it cannot expand. These problems do not exist in any bead foam process.

Therefore, those skilled in the art would recognize that Hammel and Shinohara describe different processes, and are non-analogous art. One would not look to a reference relating to a bead foam process for guidance as to how to operate an extrusion foaming operation.

As already mentioned, there is other art, not cited by the examiner, which highlights

the difficulties of extrusion foaming polylactide resins, and which shows failed attempts to increase carbon dioxide levels in an extrusion process. JP 2002-322,309A describes such a failed attempt; when 4.5% of carbon dioxide was used in a poly(lactic acid) extrusion process, poor quality foam was obtained (Comparative Example 2, paragraphs [0041] and [0042]). The foam collapsed. Not only is this art closer than either of the cited references, but it squarely discourages using high levels of carbon dioxide as a blowing agent, when extrusion foaming a poly(lactic acid).

5. The invention of claim 24 is not obvious over the combination of Hammel and Shinohara

Claim 24 is drawn to an extruded polylactide foam which has a crystallinity of about 13-24 J/g, and which is made by the process of claim 27.

One skilled in the art will readily recognize that Hammel does not describe crystalline foams. There are several reasons for this:

1) The poly(lactic acid) resins Hammel describes contain significant quantities of both L- and D-lactic acid units. *See* column 4 lines 31-33. This tends to make the resin resistant to crystallization. For example, the present application describes polylactides of this type as being “amorphous” grades. *See* the specification, page 3 lines 20-22.

2) Crystallinity is not an inherent property of foamed polylactide resins, or even of an unfoamed polylactide resin. Instead, the crystallinity of any particular polylactide article (whether it be a foam or in some other form) depends on many factors, including certain attributes of the resin itself, and the presence of other materials, but just as importantly if not more so, on the thermal history of the article. Therefore, the manner in which the article is manufactured bears heavily on its crystallinity.

The applicants discuss the effect of heat history at pages 10-11 of their specification. As is clearly stated there, crystallization is not an inherent part of the extrusion foaming process. To the contrary, crystallization develops mainly in a subsequent heat-annealing step. In Example 4, applicants show that extruded polylactide foam does not inherently have a crystallinity of from 13 to 24 J/g, even when made using large quantities of CO_2, as in this invention. Note further that the heat-annealing step, through which crystallinity is developed, takes a certain amount of time, because polylactides tend to crystallize slowly. As pointed out on page 11 lines 2-5 of applicant’s specification, it often takes more than two minutes to develop more than 10 J/g of crystallinity in an extruded polylactide foam.

3) Hammel describes no process steps which would allow crystallinity to develop in his foam. The only post-extrusion heating step that Hammel describes is a stamping step, in which the extruded foam is formed into shaped articles such plates. Operations of these expose the foam to elevated temperatures for very short times, as short cycle times are needed for processes of this type to be practiced economically.
4) The good ability to crystallize foams that is seen with this invention is attributed to the presence of a large amount of carbon dioxide during the foaming process, together with low extrusion temperatures. As described on page 10 lines 19-26, these conditions are believed to contribute to the ability of the foam to be subsequently crystallized, by plasticizing the resin and allowing it to orient during the expansion step. This orientation strengthens the foam structure and forms nucleation sites that permit future crystallization when the foam is later heat annealed. Hammel, on the other hand, does not describe these or similar conditions which would promote the ability to crystallize the foam.
5) Hammel himself says nothing about the crystallinity of the foam.

Shinohara is cited by the examiner as showing foams that have greater than 15 J/g of crystallinity. However, the portions of Shinohara which relate to crystallinity (paragraphs [0011] and [0012] apply to the resin by itself, not to the ultimate foam. Shinohara says nothing about the crystallinity of the final foam product. And as discussed before, Shinohara has no relevance at all to extruded foams or extruded foam processes.

<u>6. The invention of claims 28 and 29 is not obvious over the combination of Hammel and Shinohara</u>

Claims 28 and 29 require a post-extrusion heat treatment step to induce crystallinity into the foam. As already mentioned in the discussion of claim 24, Hammel does not teach or describe such as step. Neither does Shinohara. Therefore, claims 28 and 29 are patentable over the combination of Hammel and Shinohara for that additional reason.

<u>7. The invention of claim 30 is not obvious over the combination of Hammel and Shinohara</u>

Claim 30 requires from 7 to 11% of carbon dioxide. Hammel does not describe using more than 5% of *any* blowing agent, and clearly does not teach or suggest using 7 to 11% of

carbon dioxide. Shinohara does not relate to extrusion foaming processes at all. Therefore, claim 30 is patentable over the combination for this additional reason.

8. The invention of claim 31 is not obvious over the combination of Hammel and Shinohara and further in view of USP 5,238,968 (Morita)

Claim 31 is not obvious over the combination of these three references, for the same reason stated in section 4 above.

As already discussed, Hammel does not describe any carbon dioxide loadings in excess of 0.44, and certainly does not suggest using at least 5% by weight carbon dioxide. Shinohara relates to a different type of foaming process and is not relevant to an extrusion foaming process. Also, as discussed before, other prior art reports a failure to make good foam in an extrusion foaming process, when 4.5% carbon dioxide was used.

Morita does not overcome the deficiencies of this other art. Although Morita describes blowing agent amounts of as much as 10%, based on resin weight, this teaching takes into account the wide range of blowing agents of different types, including reactive solid, liquid and gaseous types, which Morita describes. There is nothing in Morita to lead one to select any specific quantity of carbon dioxide to use. As already discussed, those skilled in the art will recognize that molecular weight and possibly other factors contribute to the selection of blowing agent amounts; Morita cannot be fairly said to teach or suggest using at least 5% by weight of carbon dioxide specifically.

Therefore, Morita does not overcome the basic deficiencies of the other references, and claim 31 is patentable over the cited art for the same reasons as claims 27-29 and 32.

Conclusion and Request for Relief

The invention as set forth in the appended claims defines subject matter that is not obvious over the various combinations of reference cited by the examiner. The Board is respectfully requested to reverse the rejection of claims 24 and 27-32 of this application.

Respectfully submitted,
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Claims Appendix

24. An extruded foam prepared according to the process of claim 28 wherein the foam has a crystallinity of about 13-24 J/g, as measured by differential scanning calorimetry.

27. A process that comprises forming a pressurized, molten mixture of a melt-processable polylactide resin containing about 5 to about 15% by weight, based on the weight of the polylactide resin, of carbon dioxide, and extruding the molten mixture at an extrusion temperature through a die to a region of reduced pressure such that the carbon dioxide expands and the polylactide resin simultaneously cools to form a stable foam having at least 70% closed cells, wherein the polylactide resin contains at least 80% by weight polymerized lactic acid units.

28. The process of claim 27, comprising the further step of heat treating the foam to induce crystallinity.

29. The process of claim 28, wherein the polylactide resin contains a mixture of L- and D- enantiomers and the mixture of L- and D- enantiomers includes from about 85-96% by weight of one enantiomer and about 4-15% by weight of the other enantiomer.

30. The process of claim 27, wherein the pressurized, molten mixture contains 7-11% by weight by weight CO_2, based on the weight of the polylactide resin in the mixture.

31. The process of claim 27, wherein the extrusion temperature is from about 70 to about 140°C.

32. The process of claim 27 wherein the PLA resin contains long-chain branching.

Evidence Appendix

PATENT ABSTRACTS OF JAPAN

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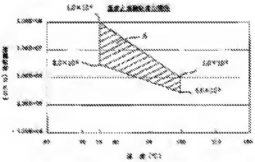
(54) **POLYLACTIC ACID RESIN FOAM AND METHOD FOR PRODUCING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a good-quality polylactic acid resin foam having a uniform and fine foam, particularly a foam of high magnification and high closed cell ratio by the extrusion foaming of the polylactic acid resin.

SOLUTION: The extrusion foaming is carried out by selecting and using the amorphous polylactic acid resin having a melt viscosity ranging from 1.0×108 to 3.0×106 PaS at 75°C and ranging from 1.0×106 to 3.0×105 PaS at 100°C, and by using a hydrocarbon and carbon dioxide as foaming agents.



[Claim(s)]

[Claim 1]Melt viscosity is within the limits of 3.0x10$^{6\text{from } 1.0\text{x}108}$ PaS in 75 **, A manufacturing method of polylactic acid system resin foam which fuses polylactic acid system resin of amorphism nature which is within the limits of 3.0x10$^{5\text{from } 1.0\text{x}106}$ PaS in 100 ** within an extrusion machine, presses hydrocarbon and carbon dioxide fit in this as a foaming agent, and is characterized by performing extrusion foaming.
[Claim 2]A manufacturing method of the polylactic acid system resin foam according to claim 1 characterized by rates of hydrocarbon and carbon dioxide of occupying being 90 to 50 % of the weight, and 10 to 50 % of the weight, respectively into a foaming agent.
[Claim 3]A manufacturing method of the polylactic acid system resin foam according to claim 1 or 2 making resin temperature when extruding from an extrusion machine into temperature within the limits of 75-100 **.
[Claim 4]Melt viscosity is within the limits of 3.0x10$^{6\text{from } 1.0\text{x}108}$ PaS in 75 **, Polylactic acid system resin of amorphism nature which is within the limits of 3.0x10$^{5\text{from } 1.0\text{x}106}$ PaS in 100 ** is fused within an extrusion machine, Polylactic acid system resin foam to which a rate of a closed cell which presses hydrocarbon and carbon dioxide fit in this as a foaming agent, made carry out extrusion foaming, and was obtained is characterized by density being 30-90-kg/m^3 at not less than 50%.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to polylactic acid system resin foam and a manufacturing method for the same.

[0002]

[Description of the Prior Art]Polylactic acid system resin is known as resin which is easy to carry out biodegradation. That is, it is said that it will be automatically decomposed during a little less than one year, and polylactic acid system resin will mainly become water and a harmless thing like carbon dioxide if this is buried underground, for example. For this

reason, polylactic acid system resin has come to be recently brought into the limelight suddenly as resin which serves as garbage forever like the conventional plastic, and does not remain, therefore does not pollute environment.

[0003]Although lactic acid may mean beta-hydroxypropionic acid rarely, an alpha hydroxypropionic acid shall usually be pointed out to it. Since the alpha hydroxypropionic acid contains the asymmetric carbon atom in the molecule, optical activity is shown, therefore three sorts of things, D-object, L-object, and racemate (D, L-object), exist in this acid. Therefore, the polylactic acid produced by polymerizing this acid becomes what differed [that it is various and] in character according to the mixing ratio of these three sorts of things, and the difference of a polymerization method etc. In fact, there are various things from which character differed greatly from the crystalline thing to the thing of amorphism nature in polylactic acid.

[0004]Commercially, polylactic acid is still in a trial production stage, and cannot be obtained easily in a commercial scene. At present, although it can obtain as a sample, if the physical properties of the sample are not clarified in many cases and result in the manufacturing method, they are in the state which is not known at all.

[0005]Since the tension of polylactic acid at the time of melting is low, it is supposed that it is it resin which is hard to make it foam. Therefore, about the foaming method of polylactic acid, what has indicated this is little. It has proposed that JP,2000-7815,A adds a thickener to polylactic acid, extrudes this, makes it foam, and considers it as foam in order to carry out that it is easy to make polylactic acid foam. Although it is explaining that this gazette can use various organic compounds as a thickener, in the example, an inorganic substance like boric acid is only used, and it is not explained at all what kind of melt viscosity it should make. Although it is explaining that this gazette can use various organic compounds as a foaming agent, carbon dioxide is only used in the example. Although the example has indicated that it was able to be made to foam 17 to 22 times, if the above-mentioned thing was used for the thickener and the foaming agent, it is very difficult to make it foam to about 20 times.

[0006]In order to carry out that it is easy to make polylactic acid foam, JP,2000-7816,A

added the inorganic filler and the foaming auxiliary to polylactic acid, and has proposed carrying out extrusion foaming. Although it is explained as an inorganic filler that various things, such as silica and zeolite, can be used, it is explained that metallic soap like calcium stearate can be used as a foaming auxiliary and it is explained that still more nearly various organic matters as a foaming agent can be used, In the example, carbon dioxide is only used as calcium stearate or calcium montanate, and a foaming agent as talc and a foaming auxiliary as an inorganic filler. Therefore, the foam obtained in the example remains in the low thing of 5.8 to 6.4 times in expansion ratio.

[0007]

[Problem(s) to be Solved by the Invention]It was difficult to have made polylactic acid foam to high magnification easily as mentioned above in a conventional method. Then, this invention tends to provide the method of obtaining easily and certainly the good polylactic acid foam to which it foamed uniformly minutely and especially the rate of a closed cell foamed to high magnification highly by improving the fault of the above conventional technologies, extruding polylactic acid and making it foam.

[0008]

[Means for Solving the Problem]In order to solve above-mentioned SUBJECT, this artificer put various polylactic acid into an extrusion machine, pressed various foaming agents fit within an extrusion machine, extruded under various extrusion conditions, foamed, and considered synthetically relation between a foaming agent and extrusion conditions. As a result, in order to make polylactic acid foam to high magnification certainly and easily, maintaining melt viscosity of polylactic acid, as it is in a certain within the limits has noticed that it is more important than anything.

[0009]A manufacturer of polylactic acid exhibits physical properties slightly about manufactured self polylactic acid. The physical properties currently exhibited have a main numerical value of mechanical properties, such as that distinction which polylactic acid is a crystalline thing or is a thing of amorphism nature, flexural strength, density, and are not released at all about the thermal characteristic especially the melting point, or melt viscosity of polylactic acid. [tensile strength, and] Therefore, this artificer measured melt viscosity about a product of each company. As a result, since crystalline polylactic acid is

rapidly fused near the crystalline melting point compared with polylactic acid of amorphism nature and reduced viscosity, it found out that it was not suitable for carrying out extrusion foaming.

[0010]Then, the melting characteristic was further examined about polylactic acid of amorphism nature. As a result, polylactic acid of amorphism nature found out that melt viscosity between about 75 ** and 100 ** was important, in order to extrude polylactic acid of amorphism nature and to have made it foam, since it was while a glass transition point was about 50-65 **.

[0011]Then, a cupping test was done about further various kinds of amorphous polylactic acid, temperature of polylactic acid was at least 75 ** and a maximum of 100 **, melt viscosity of polylactic acid at the intermediate temperature was measured, and it strove for specification of melt viscosity of polylactic acid suitable for foaming. As a result, polylactic acid found out that extrusion foaming became easy, when a related curve of the melt viscosity and temperature was within the limits of specification.

[0012]Here, a specific relation is a relation that a melt viscosity curve must exist in the shadow area A in drawing 1, when temperature expressed with a horizontal axis by Centigrade is taken, melt viscosity of polylactic acid which expressed with a vertical axis by a Pascal second (PaS) is taken and a melt viscosity curve is made. The shadow area A has melt viscosity within the limits of $1.0x10^8$PaS to $3.0x10^6$PaS in 75 **, and what is within the limits of $1.0x10^6$PaS to $3.0x10^5$PaS in 100 ** is shown.

[0013]Since viscosity of polylactic acid usually fell with a rise of temperature, when it specified melt viscosity at 75 ** and 100 ** as mentioned above, melt viscosity at an intermediate temperature between 75 ** and 100 ** checked existing between a line which connects a peak price of both-ends temperature, and a line which connects the minimum value.

[0014]An above-mentioned relation is being able to say also about a copolymer of polylactic acid and lactic acid. Here, a copolymer of lactic acid has referred to a copolymer of lactic acid and aliphatic hydroxycarboxylic acid other than lactic acid.

[0015]By the way, there is almost nothing that the melt viscosity enters in the shadow area A of drawing 1 in a sample of polylactic acid at present. Almost all samples have viscosity far higher than what enters in the shadow area A. This is clear by JP,2000-7815,A and the 2000 No. -7816 gazette. It is because a cylinder temperature is made into 170 to 180 **, it holds in an example of these gazettes to a high temperature to which T-die temperature is said as 140 ** and extrusion foaming is performed.

[0016]Therefore, this invention choosing and using polylactic acid system resin with a melt viscosity curve of amorphism nature into the shadow area A shown in drawing 1, and extruding this and making it foaming is not made so far.

[0017]If a mixture of hydrocarbon and carbon dioxide like butane is used as a foaming agent when this artificer extrudes polylactic acid system resin with a melt viscosity curve which enters in the shadow area A as mentioned above and makes it foam, It found out that good foam which foamed to high magnification with a high rate of a closed cell could be obtained easily and certainly rather than a case where other foaming agents are used when each is used independently. This invention is completed based on such knowledge.

[0018]This invention has melt viscosity within the limits of 3.0x10$^{6\text{from } 1.0\text{x}108}$ PaS in 75 **, Polylactic acid system resin of amorphism nature which is within the limits of 3.0x10$^{5\text{from } 1.0\text{x}106}$ PaS in 100 ** is fused within an extrusion machine, A manufacturing method of polylactic acid system resin foam which presses hydrocarbon and carbon dioxide fit in this as a foaming agent, and is characterized by performing extrusion foaming is provided.

[0019]Since polylactic acid system resin is resin which is hard to make it foam as mentioned above, it is difficult to make this resin foam uniformly, furthermore it is much more difficult to make this resin foam so that air bubbles may become detailed. However, polylactic acid system resin foam obtained by this invention method, Have the equal air bubbles within the limits of 0.1-0.5 mm, and it follows, It should have the low density which foams to high magnification further and it is not only the good foam to which it foamed uniformly minutely, but is called 30-90kg/m^3. This artificer found out that especially a rate

of a closed cell was a high thing which it especially says is not less than 85% not less than 50%.

[0020]Therefore, in 75 ** melt viscosity this invention, In [are within the limits of $3.0x10^{6from\ 1.0x10^8}$ PaS, and] 100 **, Polylactic acid system resin foam which extrudes polylactic acid system resin of amorphism nature which is within the limits of $3.0x10^5$PaS, made it foam, and was obtained from $1.0x10^6$ and to which it foamed uniformly minutely is provided. This invention is a low value which foams to high magnification and density calls 30-90kg/m^3 also among the above-mentioned foam, and provides unique foam in which a rate of a closed cell moreover had a high value of not less than 50%.

[0021]By this invention method, melt viscosity was measured by following methods. A melting extension flow measuring device (Oriental energy machine company make, Mertens rheometer) was used for measurement. What was fabricated to a cylindrical shape 8.5 mm in diameter and 180 mm in height was used for a test sample. After checking that the sample was immersed in an oil bath (75 ** and 100 **) for 10 minutes, and the whole sample has become a uniform temperature, they are rate of strain 0.1S $^{-\ Extension\ viscosity\ 1\ second\ after\ using\ 1}$ and beginning to pull was made into melt viscosity. A cell diameter was measured based on ASTMD-2842-69.

[0022]In this invention, polylactic acid system resin of amorphism nature in which a melt viscosity curve of resin enters in the shadow area A of drawing 1 is chosen and used, It is important to press hydrocarbon and carbon dioxide fit in resin fused within an extrusion machine, and the rest is extruded, keeps desirable 75-100 ** of resin temperature at the time within the limits of 80-95 **, and performs extrusion foaming. In addition, in order to carry out that it is easy to make it foam, it is the same as extrusion foaming of conventional resin that various foaming nucleating additives and foaming auxiliaries may be added.

[0023]By this invention, a mixture of hydrocarbon and carbon dioxide is used as a foaming agent because foam it is not only easy to make polylactic acid system resin foam uniformly minutely, but obtained when that mixture was used becomes what foamed to high magnification with a high rate of a closed cell and intensity becomes an adiathermic good large thing. As hydrocarbon, it is suitable to use aliphatic hydrocarbon, such as ethane,

propane, butane, pentane, hexane, ethylene, propylene, and petroleum ether. Even when these hydrocarbon is independent, it has the capability in which polylactic acid system resin is made to foam, but foam obtained by single use of hydrocarbon has breathability which becomes what has a low rate of a closed cell, therefore air bubbles opened for free passage mutually. For this reason, obtained foam becomes a thing with low heat insulation nature which has a weak mechanical strength. However, if hydrocarbon and carbon dioxide are used as a foaming agent, a rate of a closed cell will be highly rich in adiathermancy, and obtained foam will become what has large intensity.

[0024]Although above-mentioned ethane, propane of hydrocarbon used as a foaming agent by this invention, etc. may be independent, it may be mixtures, such as ethane and propane. Especially among hydrocarbon, butane is preferred. In this invention, what added a small amount of halogenated aliphatic hydrocarbon, nitrogen, etc., such as a methyl chloride and an ethyl chloride, further can be used for hydrocarbon and carbon dioxide as a foaming agent.

[0025]It is preferred that rates of hydrocarbon and carbon dioxide of occupying are 90 to 50 % of the weight and 10 to 50 % of the weight in a foaming agent in this case, respectively. Still more desirable rates are 90 to 70 % of the weight, and 10 to 30 % of the weight. If a foaming agent contains hydrocarbon and carbon dioxide at such a rate, the reason, It is because there is little contraction of resin after extrusion foaming, a cave stops generating to foam produced by foaming not only becoming easy, but foaming within a metallic mold being prevented by carbon dioxide, and a rate of a closed cell becomes high, therefore foam becomes heat insulation nature and the thing whose mechanical strength improved.

[0026]As a foaming nucleating additive, fines of publicly known inorganic matter which serves as a core of foaming, or an organic substance can be added. As an inorganic substance, talc, silica, etc. can be used, for example. It can be made to foam smoothly by added and extruding metallic soap, such as calcium stearate, as a foaming auxiliary. In addition, colorant, an antioxidant, etc. can also be added according to the purpose.

[0027]

[Effect of the Invention]Since polylactic acid system resin with melt viscosity which has a

melt viscosity curve in the shadow area A of drawing 1 of amorphism nature is used according to this invention method, Since the resin which has melt viscosity within the limits of 3.0x10^{6}from 1.0x10^{8} PaS in 75 **, and has it within the limits of 3.0x10^{5}from 1.0x10^{6} PaS in 100 ** will be used if it resays, When this is extruded and is made to foam at the temperature of 80-95 ** preferably 75-100 ** within an extrusion machine, polylactic acid system resin will have melt viscosity suitable for foaming. Therefore, according to this invention method, the good polylactic acid system resin foam which foamed to high magnification can be obtained easily and certainly. Since the mixture of hydrocarbon and carbon dioxide is used as a foaming agent, it extrudes, and the obtained foam foams uniformly minutely foaming not only becomes easy, but, and it becomes what has a large rate of a closed cell, therefore heat insulation nature becomes a good thing which has a large mechanical strength. At this point, this invention method gives big profits.

[0028]It is the feature to foam uniformly [the polylactic acid system resin foam obtained by this invention] minutely. It has the equal air bubbles within the limits whose average cell diameter is 0.1-0.5 mm as foaming uniformly minutely. It is especially preferred that it is a thing within the limits of 0.15-0.25 mm. Density becomes 30-90kg/m^3 and the thing which gathered uniformly by the low density 40-60kg/m^3, especially, and, as for this foam, the rate of a closed cell becomes not less than 85% of especially high thing not less than 50%. Therefore, especially as for this foam, 0.03 or less W/mk of thermal conductivity become a low thing of 0.027 or less W/mk. And this foam is obtained as a big thing with a thickness of several 10 mm and a width of hundreds of mm. Therefore, this foam can be used for various uses.

[0029]An example and a comparative example are given to below and the details of this invention method are explained. Although the rate of a closed cell and the rate of an open cell were measured about the obtained foam in the example and the comparative example, these measurement is performed based on ASTM D-2856-70 so that it may state below. That is, except for the epidermis portion of foam, five specimens which cut foam to 25 mm squares were prepared first. As a measuring device, the air relation hydrometer 1000 type (made by Tokyo Saiensu-Sha) was used. Subsequently, the value obtained by measuring the rate of a closed cell and the rate of an open cell of a specimen based on ASTMD-2856-70 was averaged, and it was considered as each value.

[0030]Although thermal conductivity was measured, it was measured based on JIS A 1412. That is, what passed for two months from the manufacturing date of foam was cut in 25 mm in thickness, 200 mm in length, and width of 200 mm, it was considered as the specimen, the heat flow which passes this specimen was measured with the monotonous heat flux meter of two sheets, and the temperature gradient of the specimen at that time was measured. The obtained heat flow and the value calculated from the temperature gradient were made into thermal conductivity.

[0031]

[Work example 1]As resin, the melt viscosity at 75 ** is 1.0x10^7PaS, and the polylactic acid of amorphism nature adjusted so that the melt viscosity at 100 ** might be 6.0x10^5PaS was used. The glass transition point of this resin was 53 **. The mixture obtained by adding high DOROSE roll CF(made in Bex Linger) 0.3 weight section to this resin 100 weight section was supplied to the tandem extrusion machine (50 to 60 mm caliber). While carrying out melting kneading of the resin within the 1st extrusion machine, as a foaming agent, butane is 5.0 weight sections and carbon dioxide is 1.0 weight sections, 83.3% of the weight, the rate that the carbon dioxide in a foaming agent occupies presses fit the thing used as 16.7 % of the weight, and the rate that the butane in a foaming agent occupies sends this to the 2nd extrusion machine, and cools resin temperature to 84 ** within the 2nd extrusion machine, It was made to extrude and foam under pressure 12MPa from 2 mm of slits, and a 90-mm-wide cap.

[0032]The cell diameter foamed to the obtained foam uniformly minutely at an average of about 0.20 mm, and density was a good thing which are 41.2kg/m^3, 28 mm in thickness, and 215 mm in width. The rate of an open cell is low, this foam was 6.4%, and the rate of a closed cell was 90.5%. Thermal conductivity was 0.0262 W/mk.

[0033]

[Work example 2]As resin, the melt viscosity at 75 ** is 1.0x10^7PaS, and the melt viscosity at 100 ** used amorphous polylactic acid which is 6.0x10^5PaS. The glass transition point of this resin was 53 **. In butane, 3.8 weight sections and carbon dioxide to 100 copies of this resin in the amount part of duplexs. It carried out completely like Example 1, extruded, and

was made to foam except the rate that the butane in a foaming agent occupies having decided that the rate that the carbon dioxide in a foaming agent occupies presses fit the thing used as 34.5 % of the weight, and extrudes with the resin temperature of 87 ** 65.5% of the weight.

[0034]The cell diameter foamed to the obtained foam uniformly minutely at an average of 0.18 mm, and density was a good thing which are 44.3kg/m^3, 27 mm in thickness, and 220 mm in width. The rate of an open cell of this foam was 5.9%, and the rate of a closed cell was 91.2%. Thermal conductivity was 0.0258 W/mk.

[0035]

[Work example 3]As resin, the melt viscosity at 75 ** is 1.0x10^7PaS, and the melt viscosity at 100 ** used amorphous polylactic acid which is 6.0x10^5PaS. The glass transition point of this resin was 53 **. In butane, 3.0 weight sections and carbon dioxide to 100 copies of this resin by 2.5 weight sections. Extrusion foaming was carried out completely like Example 1 except the rate that the butane in a foaming agent occupies having decided that the rate that the carbon dioxide in a foaming agent occupies presses fit the thing used as 45.5 % of the weight, and extrudes this at 90 ** 54.5% of the weight.

[0036]The cell diameter is foaming to the obtained foam uniformly minutely at 0.15 mm. Density was a good thing which are 47.1-kg/m^3, 26 mm in thickness, and 222 mm in width. The rate of an open cell of this foam was 5.5%, the rate of a closed cell was 91.5%, and thermal conductivity was 0.0255 W/mk.

[0037]

[Work example 4]As resin, the melt viscosity at 75 ** is 3.0x10^7PaS, and the melt viscosity at 100 ** used amorphous polylactic acid which is 9.0x10^5PaS. The glass transition point of this resin was 54 **. In butane, 5.0 weight sections and carbon dioxide to this resin 100 weight section by 1.0 weight sections. Extrusion foaming was carried out completely like Example 1 except the rate that the butane in a foaming agent occupies having decided that the rate that the carbon dioxide in a foaming agent occupies presses fit the thing used as 16.7 % of the weight, and extrudes this at 90 ** 83.3% of the weight.

[0038]The cell diameter was foaming to the obtained foam uniformly minutely at 0.23 mm, and density was a good thing which are 44.0kg/m^3, 28 mm in thickness, and 214 mm in width. The rate of an open cell of this foam was 6.7%, the rate of a closed cell was 89.9%, and thermal conductivity was 0.0265 W/mk.

[0039]

[Comparative example 1] As resin, the melt viscosity at 75 ** is 7.0x10^{8}PaS, and the melt viscosity at 100 ** used amorphous polylactic acid which is 2.0x10^{6}PaS. The glass transition point of this resin was 55 **. Butane 6.5 weight section is pressed fit in this resin 100 weight section, and it extruded completely like Example 1 and was made to foam except having decided that resin temperature shall be 78 ** and is extruded.
[0040]In this method, it contracted, after the extruded resin foaming, and density became 122 kg/m^3, and very heavy good foam was not obtained.

[0041]

[Comparative example 2] As resin, the melt viscosity at 75 ** is 3.0x10^{7}PaS, and the melt viscosity at 100 ** used amorphous polylactic acid which is 9.0x10^{5}PaS. The glass transition point of this resin was 53 **. Carbon dioxide 4.5 weight section is pressed fit in this resin 100 weight section, and it extruded completely like Example 1 and was made to foam except having decided that resin temperature shall be 98 ** and is extruded.

[0042]The cave occurred inside and the obtained foam did not turn into good foam.

[0043]

[Comparative example 3] As resin, the melt viscosity at 75 ** is 7.0x10^{8}PaS, and the melt viscosity at 100 ** used amorphous polylactic acid of 2.0x10^{6}PaS. The glass transition point of this resin was 53 **. 5.0 weight sections and 1.0 weight sections of carbon dioxide are pressed fit in this resin 100 weight section for butane, and it extruded completely like Example 1 and was made to foam except having decided that resin temperature shall be 101 ** and is extruded.

[0044]The obtained foam did not have constant shape, and variation was large and density's was not good.

[0045]

[Comparative example 4] As resin, the melt viscosity at 75 ** is $8.0x10^5$PaS, and the melt viscosity at 100 ** used amorphous polylactic acid of $1.0x10^5$PaS. The glass transition point of this resin was 53 **. 1.0 weight sections are pressed fit in this resin 100 weight section for butane 5.0 weight section and carbon dioxide, and it extruded completely like Example 1 and was made to foam except having decided that resin temperature shall be 78 ** and is extruded.

[0046]The obtained foam did not have constant shape, and variation was large and density's was not good.

Related Proceedings Appendix

(none)